

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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Rapid Column Extraction Method for Actinides in Soil

Sherrod L. Maxwell, III and Brian K. Culligan

Sherrod L. Maxwell

Westinghouse Savannah River Company

Building 735-B

Aiken, SC 29808, USA

phone #: 803-952-7473

Fax#: 803-952-7881

Email: sherrod.maxwell@srs.gov

Abstract

The analysis of actinides in environmental soil and sediment samples is very important for environmental monitoring as well as for emergency preparedness. A new, rapid actinide separation method has been developed and implemented that provides total dissolution of large soil samples, high chemical recoveries and effective removal of matrix interferences. This method uses stacked TEVA Resin[®], TRU Resin[®] and DGA-Resin[®] cartridges from Eichrom Technologies (Darien, IL, USA) that allows the rapid separation of plutonium (Pu) neptunium (Np), uranium (U), americium (Am), and curium (Cm) using a single multi-stage column combined with alpha spectrometry. The method combines a rapid fusion step for total dissolution to dissolve refractory analytes and matrix removal using cerium fluoride precipitation to remove the difficult soil matrix. By using vacuum box cartridge technology with rapid flow rates, sample preparation time is minimized.

Key Words

Soil

Sediments

Actinide analysis

Extraction chromatography

Actinide separations

Resin

Introduction

The analysis of actinides in environmental soil samples is an important analysis to meet environmental monitoring requirements at the Department of Energy's Savannah River Site (Aiken, South Carolina, USA). Soil and sediment samples are analyzed at the Savannah River Site as part of a routine surveillance program. There is also a growing need to have available rapid methods to accurately assess actinides in environmental soil and sediment samples for emergency preparedness reasons (1, 2). A preconcentration method using Diphonix Resin® (Eichrom Technologies, Darien, IL, USA) for large soil samples was previously reported by this laboratory (3). Although this method successfully removed soil matrix interferences, it required a microwave dissolution of the Diphonix Resin® to remove the actinides. The microwave dissolution steps could be time-consuming, depending on the performance of the microwave. Actinides can be removed

from Diphonix Resin using 1-hydroxyethane-1, 1-diphosphonic acid (HEDPA) extractant. The HEDPA extractant can be destroyed via a manual hot plate digestion prior to further analysis, but this method generates a large amount of residual phosphate and often requires much larger extraction columns to separate the actinides. (4)

A new matrix removal technique was developed in the SRS Environmental Laboratory that is simpler and more effective than the Diphonix Resin methods. After a fusion technique to provide complete dissolution of the soil matrix and an iron hydroxide precipitation to collect the actinides, a novel cerium fluoride precipitation is used to effectively eliminate the soil matrix. This new method uses stacked TEVA Resin®, TRU Resin® and DGA-Resin® cartridges from Eichrom Technologies (Darien, IL, USA) that allows the rapid separation of plutonium, neptunium, uranium, americium, and curium using a single multi-stage column to separate actinide isotopes for alpha spectrometry. DGA-Resin®, which has very strong retention for americium and curium, is used to enhance chemical recoveries of those analytes (5).

The new SRS soil method is a rapid method that effectively separates actinides for analysis from large soil samples for routine environmental monitoring or for emergency response needs. It provides rapid, total dissolution of refractory actinides in soil samples and uses a stacked cartridge technology that allows for sequential actinides separations with minimal waste generation.

Experimental

Reagents

The resins employed in this work are TEVA Resin® (Aliquat TM336), TRU-Resin® (tri-n-butylphosphate (TBP) and N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)), DGA Resin (N,N,N',N' tetraoctyldiglycolamide), and Prefilter Resin (Amberchrome-CG-71) available from Eichrom Technologies, Inc., (Darien, Illinois). Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc.). All water was obtained from a Milli-Q2TM water purification system. All other materials were ACS reagent grade and were used as received. Radiochemical isotope tracers Pu-242, Am-243, and U-232 that were obtained from Analytics, Inc. (Atlanta, GA, USA) and diluted to the approximately 2 pCi/mL level were employed to enable yield corrections. Laboratory Control Standards (LCS) were analyzed using Pu-238, U-235, Am-241 and Cm-244 standards that were obtained from Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 2 pCi/mL.

Procedures

Column preparation. TEVA, TRU, and DGA Resin columns were obtained as cartridges containing 2 mL of each resin from Eichrom Technologies, Inc.. Small particle size (50-100 micron) resin was employed, along with a vacuum extraction system (Eichrom Technologies). Flow rates of 1 -2 mL/min were typically used, much faster than the 0.25 mL/min gravity flow rates typically observed. Sample loading and column stripping steps were performed at ~1 drop/second, while column rinse steps were usually performed at 1 to 2 drops per second.

Sample Preparation. Soil samples were dried at 110C and blended prior to taking sample aliquots. Five-gram sample aliquots were taken for soil samples that were more clay-like in texture and ten-gram aliquots were taken for sandy soil and sediment samples with high silicon content. After samples were aliquoted into 50 mL glass beakers, tracers were added and the samples were placed in a furnace at 550C for 4 hours or more. Samples were transferred to 250 mL teflon beakers, rinsing the glass beakers with hot concentrated nitric acid. Five milliliters of concentrated hydrochloric acid and 10 mL of concentrated hydrofluoric acid were added. The samples were ashed to dryness on a hotplate. For emergency response samples which require faster turnaround, the furnace step can be eliminated if ~ 2 mL of 30 wt% hydrogen peroxide is also added during each of the following ashing steps. Five mL of concentrated nitric acid and 5 mL of concentrated hydrofluoric acid were added and the samples were ashed to dryness on a hotplate. This step was repeated once more. Any residual fluoride was volatilized by adding 5 mL of concentrated nitric acid and heating to dryness on a hot plate twice. Silicon was volatilized during the ashing steps with hydrofluoric acid as SiF_6 . After ashing, the residual solids were transferred to 250 mL zirconium crucibles (Metal Technology, Inc., Albany, OR, USA). The beakers were rinsed with concentrated nitric acid, transferred to the crucible and the crucible contents were evaporated on a hot plate to dryness.

After removing the crucibles and allowing them to cool, 15 grams of sodium hydroxide were added to each crucible. The crucibles were covered with a zirconium lid and placed into a furnace at 600C for 20 minutes. Smith et al have also applied sodium hydroxide fusion to soil samples (6).

After removing the crucibles from the furnace, they were transferred to a hot plate and water was added to transfer the solids to 225 mL centrifuge tubes. The residual solids were removed from the crucibles by adding water and heating the crucibles on the hot plate as needed. One hundred and twenty-five milligrams of iron were added as ferric nitrate to each sample. Five milliliters of 20% titanium chloride were added to each tube, followed by 1 mL of 10% barium nitrate to complex any carbonate present. Seven milligrams of cerium were typically added as cerium nitrate to each tube, however only 1 mg of cerium was added to soil standards such as MAPEP laboratory soil standards that contain higher levels of rare earth elements. The tubes were centrifuged at 3500 rpm for 5 minutes and the supernate was poured off. The remaining solids were dissolved in a total volume of 60 mL of 1.5 M HCl. This solution was diluted to 170 mL with 0.01M HCL. Two milligrams of cerium as cerium nitrate were added to each sample. To ensure no actinides were in the hexavalent state and facilitate complete precipitation, ten milliliters of 20% titanium chloride were added to each sample. Twenty-two milliliters of 28M hydrofluoric acid were added to each sample. The samples were placed on ice for ~10 minutes to reduce solubility and centrifuged for 20 minutes at 3500 rpm. The supernate was removed and the residual solids containing the actinides were dissolved in 5 mL of warm 3M HNO₃-0.25M boric acid, 6 mL of 7M HNO₃ and 7.5 mL of 2 M aluminum nitrate. The solids were transferred to 100 mL teflon beakers during this step and warmed to redissolve the solids. The aluminum nitrate was previously scrubbed to remove trace uranium by passing approximately 250 mL of 2M aluminum nitrate through a large column (Environmental Express, Mount Pleasant, SC, USA) containing 7 mL of UTEVA

Resin (Eichrom Technologies) at ~10 to 15 mL per minute. The columns were prepared from a water slurry of the UTEVA Resin.

Column separation. TEVA, TRU, and DGA Resin cartridges were stacked on the vacuum box from top to bottom, in that order. Fifty milliliter centrifuge tubes were used to collect the rinse or final purified fractions.

A valence adjustment was performed by adding 0.5 mL of 1.5M sulfamic acid and 1.25 mL of 1.5M ascorbic acid. After a three-minute wait step, one milliliter of 3.5M sodium nitrite (freshly prepared) to adjust plutonium to Pu^{+4} . After the valence adjustment, the sample solution was loaded onto the stacked column at approximately 1 drop per second. After the sample was loaded, a beaker rinse of 3 mL of 6M HNO_3 was transferred to the stacked column. At this point the TRU and DGA cartridges were removed and the DGA Resin cartridges were placed on a second vacuum box. Five milliliters of 0.25M nitric acid were added to each DGA column to remove any residual uranium that may have been retained on the DGA cartridges. This rinse was collected and set aside for later addition to TRU Resin. The TEVA Resin was rinsed with 7 mL of 3M HNO_3 to remove residual uranium, which was also collected and set aside for later addition to TRU Resin. The TEVA cartridge was rinsed with 10 mL of 5M nitric acid and then 10 mL of 3M nitric acid to remove matrix components. To elute thorium from TEVA Resin, 23 mL of 9M hydrochloric acid were added.

A 5 mL volume of 3M HNO_3 was added to TEVA Resin (and discarded) to reduce the amount of any residual extractant before stripping the plutonium from the resin. The plutonium was stripped from TEVA Resin with 20 mLs of 0.1M hydrochloric acid-

0.05M hydrofluoric acid –0.03M titanium chloride (freshly prepared). A 0.5 mL volume of 30 wt% hydrogen peroxide was added to each Pu strip solution to oxidize any residual uranium to U^{+6} as a precaution to prevent coprecipitation. Fifty micrograms of cerium as cerium nitrate was added, along with 1 mL of concentrated hydrofluoric acid (49%). After waiting 30 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene and counted by alpha spectrometry .

The TRU cartridges were placed above the DGA cartridges and 15 mL of 4M HCL was used to strip Am and Cm from TRU Resin onto the DGA Resin. After removal of the TRU cartridges, the DGA cartridges were stripped with 10 mL of 0.25M HCL. These strip solutions were transferred to 50 mL glass beakers using ~3 mL of concentrated nitric acid and 0.05mL of 1.8M sulfuric acid was added to enhance destruction of any extractant in this solution. The Am/Cm strip solutions were evaporated to dryness on a hotplate. These fractions were ashed once time using 2 mLs of concentrated nitric acid and 2 mL of 30 wt% hydrogen peroxide to remove any residual extractant that may have bled off the resin. The samples were redissolved in 5 mL of 4M ammonium thiocyanate-0.1M formic acid, warming gently as needed. These solutions were loaded onto a TEVA cartridge to remove rare earths present, which interfere with alpha spectrometry peak resolution. The TEVA cartridges were rinsed with 10 mL of 1.5M ammonium thiocyanate-0.1M formic acid to remove rare earths, and the americium and curium were stripped using 20 mL of 1M HCL. The original load solution beaker was rinsed with 5 mL of warm 1M HCL to ensure all the americium and curium was removed from this beaker. This solution, followed by 15 mL of 1M HCL also used to rinse the beaker, was passed through the TEVA Resin to remove the americium and curium. Fifty

micrograms of cerium as cerium nitrate was added, along with 2 mL of concentrated hydrofluoric acid (49%). After waiting 30 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene and counted by alpha spectrometry.

Three milliliters of concentrated HNO₃ was added to each 3 M HNO₃ rinse volume from TEVA resin that was set aside and added to TRU Resin to recover any residual amount of uranium from TEVA Resin. The 0.25M HNO₃ rinse from DGA Resin was also added to TRU Resin after 4 mL of concentrated HNO₃ was added to increase the acidity of this solution to ~7M HNO₃. The higher nitric acid concentration increases the retention of uranium on TRU Resin and selects against retention of any Po-210. TRU Resin was rinsed with 18 mL of 4M HCL-0.2M HF to remove any residual thorium that may have passed through TEVA and been retained on TRU Resin. Uranium was stripped from TRU Resin using 15 mL of 0.1M ammonium bioxalate. A 0.5 mL volume of 20 wt% titanium chloride was added to reduce U to U⁺⁴. Fifty micrograms of cerium as cerium nitrate was added, along with 1 mL of concentrated hydrofluoric acid (49%). After waiting 30 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene filters (Resolve® filter-Eichrom Technologies) and counted by alpha spectrometry.

Figure 1 shows the vacuum box apparatus and the stacked TEVA, TRU and DGA Resin cartridges. The second vacuum box in the picture was used after the cartridges were split apart so that the cartridges could be processed on two boxes for enhanced productivity. DGA and TRU Resin cartridges were moved to the second box and stripped as described above.

Apparatus

Plutonium, americium, curium and uranium measurements were performed by alpha-particle pulse-height measurements using Passivated Implanted Planar Silicon (PIPS) detectors. Polycarbonate vacuum boxes with 24 positions and a rack to hold 50 mL plastic tubes were used. Two boxes were connected to a single vacuum source by using a T-connector and individual valves on the tubing to each box.

Results and Discussion

Table 1 shows tracer recoveries for a typical batch of soil samples using an aliquot of 5 grams for each sample. The results for a Laboratory Control Standard (spiked blank) analyzed along with this batch of soil samples is also shown in Table 1. The measured values for Pu-238, Am-241, Cm-244 and U-235 are well within the QC guidelines of 75%-125% of the known values. Table 2 shows results for the analysis of the refractory soil standard MAPEP-05-S13 (Department of Energy (DOE) – Radiological and Environmental Sciences Laboratory (RESL), Idaho Falls, ID, USA). The measured values are within 5% of the MAPEP reference values, indicating excellent method performance. Sill and Sill have emphasized the need for total dissolution soil methods.(7) Total dissolution allows accurate measurement of refractory particles and the large sample size

makes accurate measurement of lower levels quantities possible, as shown by the accurate measurement of the Pu-238 isotope at the ~0.5 Bq/kg level. Table 3 again shows excellent performance on a DOE-QAP soil standard 0903 (DOE-EML -Environmental Measurements Laboratory, New York, NY, USA) versus reference values. If incomplete dissolution had occurred on the refractory samples, results would have been low. Polonium-210 (5.30 MeV) has an unresolvable alpha energy from U-232 (5.26, 5.32 MeV). If Po-210 had not been removed effectively, U-232 tracer values would have been biased high and U-234 and U-238 measured values would have been biased low. Figure 2 shows a typical spectra for the plutonium isotopes when Pu-242 is used as the tracer. The Pu-242 tracer recovery was 99.5% and the Full Width Half Maximum (FWHM) was 55 keV, showing good alpha peak resolution. Figure 3 shows an example of spectra for the Am/Cm isotopes. The Am-243 tracer recovery was 105.5% and the FWHM was 48.6 keV. Figure 4 shows an example of the spectra for uranium isotopes. The U-232 tracer recovery was 108.8% and the FWHM was 38.3 keV. if Pu-236 tracer is used instead of Pu-242, neptunium can also be measured. (8, 9). To facilitate Np reduction to Np^{+4} in the column load solution, a small amount of iron (~0.5 mg) added along with the ascorbic acid is required.

After initial drying, blending and heating at 550C for 4 hours, the time required to prepare a batch of soil samples is about 5 hours. The column work usually takes about 5 to 6 hours for all the actinides to be separated and purified. The new method is much faster than the previous soil method used in the SRS Environmental Laboratory.

Conclusions

The new soil method developed in the SRS Environmental Laboratory is a rapid method for actinides that can be used for routine or emergency analyses of environmental soil samples. This method has high tracer recoveries, effectively removes interferences and combines the sample preparation for a large number of actinides into a single multi-stage column extraction method. The method provides total dissolution and effective removal of soil matrix interferences.

Acknowledgment

This work was performed under the auspices of the Department of Energy, DOE Contract No. DE-AC09-96SR18500. The authors wish to acknowledge Gene Cooke, Martha Holmes, Becky Chavous and Jack Herrington for their assistance in testing this method.

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Table Captions

Table 1 Performance of Method on Typical Soil Samples

Table 2. Performance on MAPEP-05-S13 Refractory Soil Standard

Table 3. Performance on DOE-EML QAP Soil Standard

Figure Captions

Figure 1. Vacuum Box System with Stacked Cartridges

Figure 2. Alpha Spectrometry Spectra showing Pu Isotopes

Figure 3. Alpha Spectrometry Spectra showing Am Isotopes

Figure 4. Alpha Spectrometry Spectra showing U Isotopes

Table 1. Performance of Method on Typical Soil Samples

N=7

Tracer	Avg. Recovery	RSD	LCS Recovery
Pu-242	104%	4.4%	96.2% (Pu-238)
Am-243	105.2%	5.3%	88.0% (Am-241)
U-232	98.4%	13%	95% (U-235)

Table 2. Performance on MAPEP-05-S13 Refractory Soil Standard

Analyte	Measured	Reference	Ratio
Pu-238	0.48	0.48	1.00
Pu-239	84.1	89.5	0.95
Am-241	101	109	0.93
U-234	64.9	62.5	1.04
U-238	252	249	1.01

Results in Bq/kg

5 gram sample analyzed

Results are average of 3 replicates.

Table 3. Performance on DOE-EML Soil Standard 0903

Analyte	Measured	Reference	Ratio
Pu-238	31.2	30.4	1.02
Pu-239	15.0	14.6	1.03
Am-241	17.5	18.4	0.95

U-234	125.0	127.3	0.98
U-238	126.4	127.1	0.99

Results in Bq/kg

5 gram sample analyzed

Results are average of 2 replicates.

Figure 1 Vacuum Box with Stacked Cartridges (TEVA+TRU+DGA Resin)

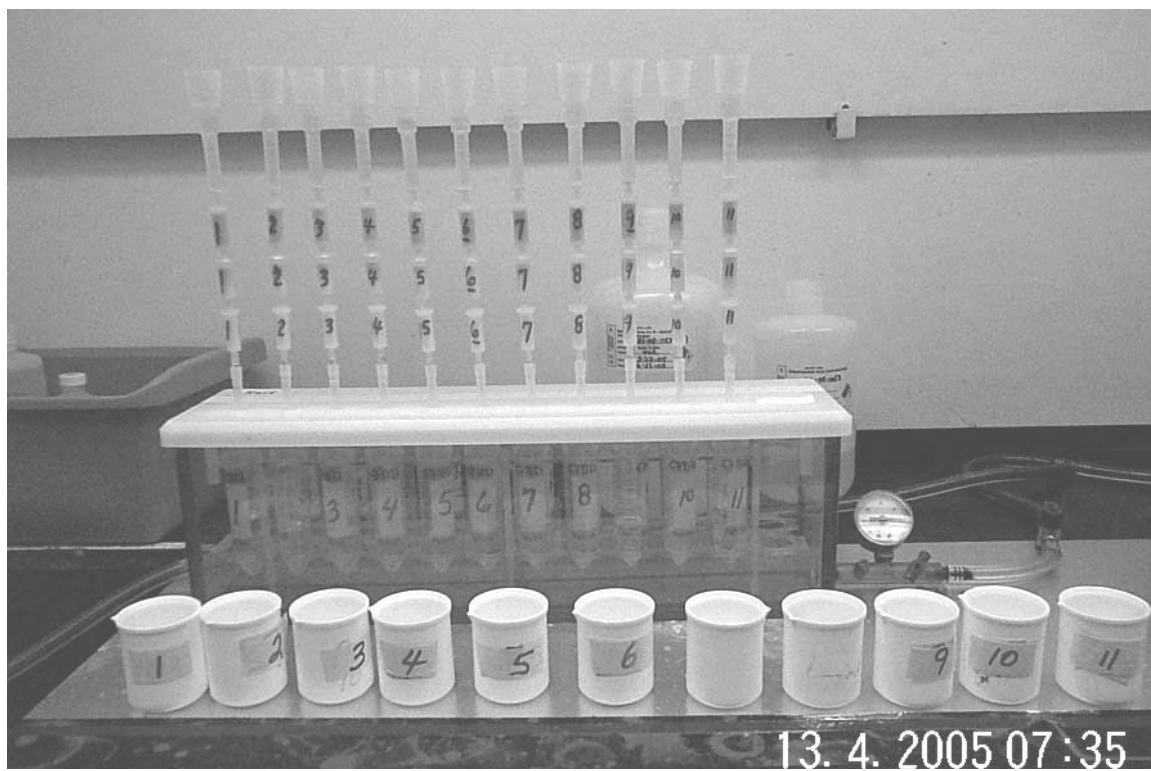


Figure 2 Alpha Spectrometry Spectra showing Pu Isotopes

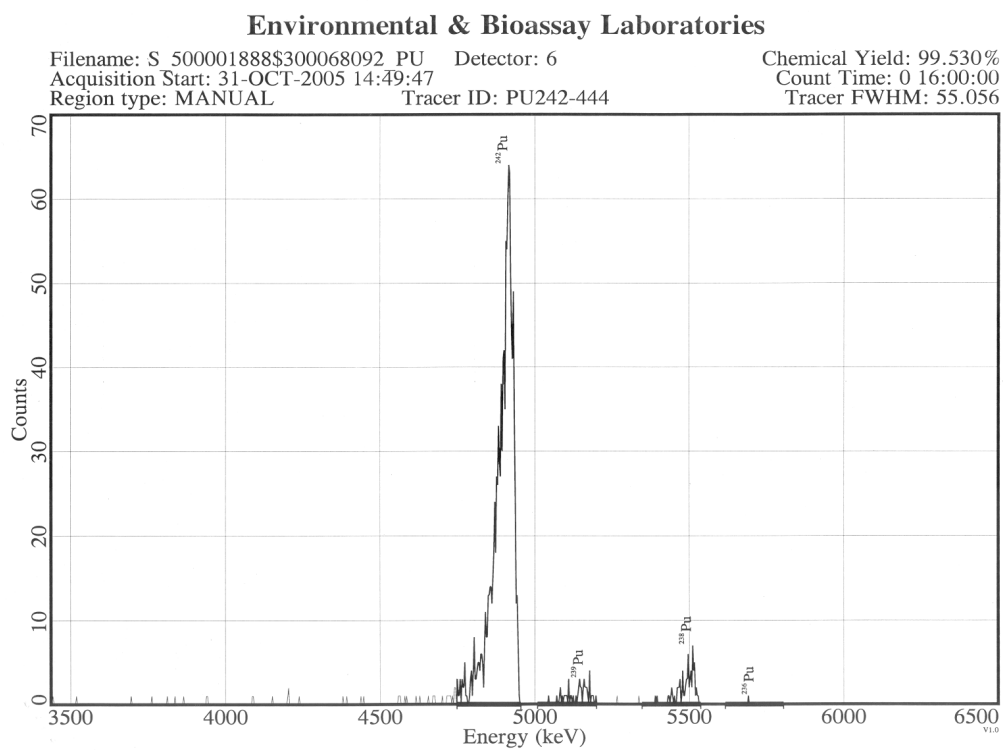


Figure 3 Alpha Spectrometry Spectra showing Am Isotopes

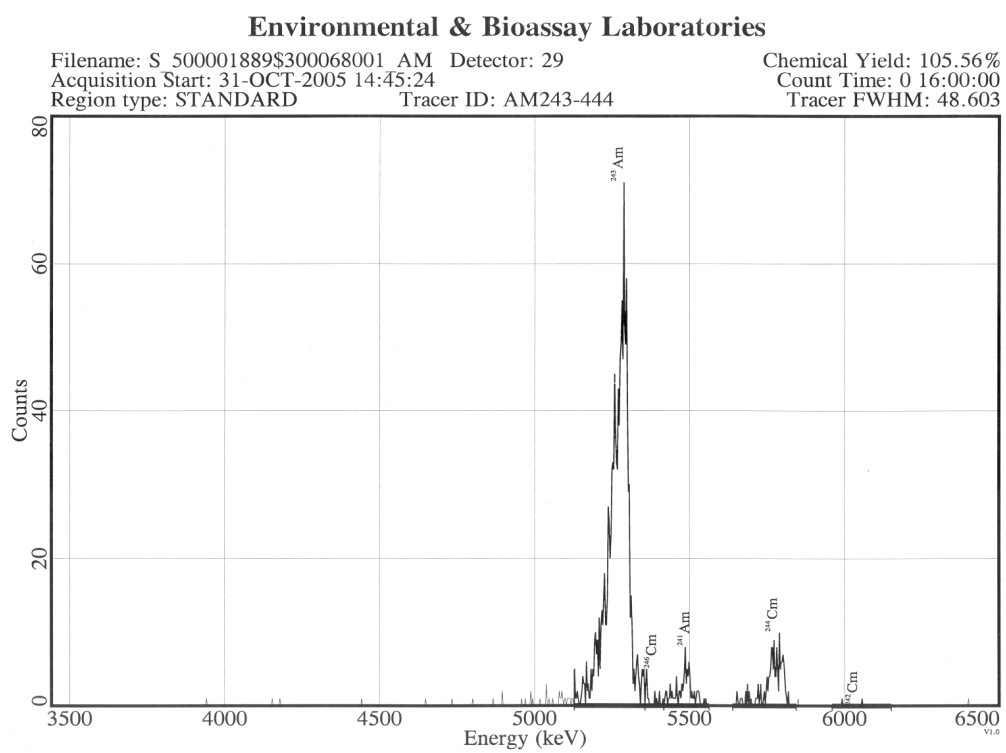


Figure 3 Alpha Spectrometry Spectra showing U Isotopes

